# Grain Boundaries in High Performance Magnets, reasons for poor or excellent properties?

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## Abstract

Advanced $Nd_2Fe_{14}B$-based permanent magnets exhibit a complex, multiphase microstructure and show the highest values of coercivity and energy density products, obtained so far. The hysteresis properties are governed by a combination of the intrinsic properties of the material, such as saturation polarisation, exchange and magnetocrystalline anisotropy. The other important factors are the microstructural parameters, such as grain size, the orientation of the easy axes of the grains and the distribution of phases. The grain size of the magnets and the alignment of the grains strongly depend on the processing parameters. The formation and distribution of the phases is determined by the composition of the magnets and the annealing treatment. The intergranular structure between the grains plays a significant role determining the magnetic properties. The coercivity is determined by the long range dipolar interaction and short range exchange coupling between neighbouring grains. The doping of elements changes the phase relation and favours the formation of new phases. Additional intergranular phases decrease the remanence and interrupt the magnetic interactions between the grains, thereby improving the coercivity of large grained sintered magnets. Non magnetic phases, which replace the Nd-rich intergranular phase, considerably improve the corrosion resistance and are of great technological interest. Exchange interactions between neighbouring soft and hard grains lead to remanence enhancement of isotropically oriented grains in nanocrystalline composite magnets. Micromagnetic finite element simulations show that the magnetic properties of the disturbed intergranular region strongly deteriorate the coercive field of the magnet. Insufficient temperature stability and poor corrosion resistance are the main factors limiting applications of $Nd_2Fe_{14}B$-based magnets.

## 1. Introduction

Hard magnetic materials are divided into the group of conventional metallic and oxide magnets and the group of modern magnets based on intermetallic compounds of rare earth elements with cobalt and/or iron. The importance of newly developed permanent magnetic materials in many electro-, magnetomechanical and electronic applications can be attributed to the drastic improvement of the magnetic energy density product and coercive field of the new hard magnetic materials. The rare earth intermetallic phases $SmCo_5$, $Sm_2Co_{17}$ [1] and $Nd_2Fe_{14}B$ [2,3] are the basis for these high performance magnets. Rare earth-Co magnets exhibit the highest coercive fields and (Nd,Dy)-(Fe,Co)-B:(M1,M2) magnets show the highest value of energy density product, obtained so far. High performance $SmCo_5/Sm_2Co_{17}$- and $Nd_2Fe_{14}B$-based permanent magnets exhibit a complex, multiphase microstructure. The grain size of the magnets and the alignment of the grains strongly depend on the processing parameters. The formation and distribution of the phases is determined by the composition of the magnets and the annealing treatment. High performance $Nd_2Fe_{14}B$-based permanent magnets are produced with different composition and various processing techniques [4,5], which influence the complex, multiphase microstructure of the magnets, such as grain size, the orientation of the easy axes of the grains and the distribution of phases:

- grain sizes in the range between 10 nm and 500 nm are obtained by melt-spinning, mechanical alloying and the HDDR (hydrogenation-disproportionation-desorption-recombination) process
- sintered and hot worked magnets exhibit grain sizes above 1 μm

For the better understanding and the further development of high performance permanent magnets and for the search of new phases a detailed understanding of the microstructure and grain boundaries is necessary. This also includes the exact knowledge of the crystallography, phase diagram and phase relation of the magnet system. The hysteresis properties are governed by a combination of the intrinsic properties of the material, such as saturation polarisation, magnetic exchange and magnetocrystalline anisotropy and the influence of the microstructure on the magnetization reversal process. The role of intergranular structure between the grains plays a significant role determining the magnetic properties, especially if the grain diameter is in the nanometer scale [6].

## 2. Experimental procedure

Highest energy density Nd-Fe-B permanent magnets (>400 kJ/m$^3$) exhibiting a low oxygen content have been prepared by the sintering route according to the following experimental procedure [7,8]. The $(Nd,Pr)_{12.6\text{-}15.1}Fe_{72.8\text{-}80.5}B_{5.8\text{-}6.1}$ alloys were strip cast in an argon atmosphere from Nd-Fe, Fe-B, Fe and (Cu,Al) pre-alloys. The crushed flakes exhibit a homogeneous microstructure of fine dispersed Nd-rich phase within a $Nd_2Fe_{14}B$ matrix phase [9]. Using the hydrogen decrepitation (HD) process coarse powders of less than 500 μm were prepared. After jet milling under nitrogen-gas atmosphere fine powders of about 2.2-3.3 μm in mean FSSS particle size (Fisher Sub Sieve Size) were obtained. The oxygen content of the milling gas was in the order of 10 ppm $O_2$. The distribution of the size of fine powders was measured with a scanning electron microscope.
The fine powders were pre-pressed and pre-aligned with a pulsed field in the glove box under argon atmosphere to a rectangular compact. The encapsled magnets were pressed in a transverse magnetic field press (combination of RIP and TDP) under a magnetic field of 1200 kA/m. This new pressing technique showed an improved alignment of the hard grains and therefore a high value of remanence. These compacts were sintered at 1233-1373 K for 10.8 ks in vacuum and were subsequently annealed at about 1073 K for 900 s and 783-843 K for 3.6 ks in order to obtain optimum density and coercive field.
Magnetic properties were measured by a B-H hysteresis tracer after being fully magnetised in a pulsed field up to 7 T. After each step of the preparation route the oxygen content of the alloy, power and the magnet, respectively was measured with a LECO oxygen analyser. The microstructure (grain size, phases and degree of alignment of grains) and the magnetic domain structure of the magnets was investigated by Kerr microscopy, electron probe microanalysis, scanning and transmission electron microscopy.

## 3. Intergranular phases in doped and substituted Nd-Fe-B magnets

Substituent and dopant elements influence the microstructure, coercivity and corrosion resistance of advanced (Nd,S1)-(Fe,S2)-B:(M1,M2) magnets. The multicomponent composition of the magnets leads to the formation of non-magnetic and soft magnetic phases. Generally, two types of substituent elements, which replace the rare earth element or the transition element sites in the hard magnetic phase, and two types of dopant elements are

distinguished [6]. Selected substituent elements replace the Nd-atoms (S1=Dy,Tb) and the Fe-atoms (S2=Co,Ni,Cr) , respectively, in the hard magnetic ϕ-phase and considerably change intrinsic properties, such as the spontaneous polarisation, the Curie temperature and the magnetocrystalline anisotropy. The main difference between substituent and dopant elements is the solubility range within the $Nd_2Fe_{14}B$ phase. Our previous, systematic TEM-studies performed on sintered, melt-spun, mechanically alloyed and hot worked magnets have shown that two different types of dopants can be distinguished independently of the processing route. Depending on the type, the dopant elements form additional intergranular rare-earth-containing or boride phases [7,8]:

- *Type 1 dopants* (M1 = Al, Cu, Zn, Ga, Ge, Sn)
  form binary M1-Nd or ternary M1-Fe-Nd phases
- *Type 2 dopants* (M2 = Ti, Zr; V, Mo; Nb, W)
  form binary M2-B or ternary M2-Fe-B phases

The doping changes the microstructure of Nd-Fe-B sintered magnets in the following way: If there exists a solubility at the high temperature (1100°C), the dopant element is partly dissolved in the hard magnetic $Nd_2Fe_{14}B$ phase. This is the case for most of the M1-dopant elements (Al and Ga). The dopant element partly replaces the Fe-atoms and therefore also changes the spontaneous polarisation, Curie temperature and anisotropy field. If the solubility at sintering temperature is low, precipitation within the 2:14:1-phase occurs. This is mainly the case with M2-dopants.

TEM investigations have been carried out in order to identify the various phases in doped and substituted $Nd_2Fe_{14}B$ based magnets. The main effect of the addition of dopant elements is the formation of new intergranular phases. In summary the following phases were identified [10]:

- *Primary hard magnetic phase:* $Nd_2Fe_{14}B$
- *Secondary phases:*
  Nd-rich liquid sintering phase
  $Nd_{1+\varepsilon}Fe_4B_4$
  M1-Nd (CuNd, $GaNd_3$, $Ga_3Nd_5$)
  M1-Fe-Nd ($M1_{1+x}Fe_{13-x}Nd_6$)
  M2-B ($TiB_2$, $ZrB_2$)
  M2-Fe-B ($V_{2-x}Fe_{1+x}B_2$, NbFeB)
  α-Fe
  Oxide-phases ($Nd_2O_3$, ..)
- *Additional* phases in Dy- and Co-substituted and M1- and M2-doped *magnets*:
  $Nd(Co,Fe)_4B$
  $Nd(Co,Fe)_2$
  $Nd_3Co$
  Dy-containing phases

Intergranular phases change the coupling behaviour between the hard magnetic grains. Non-magnetic phases eliminate the direct exchange interaction and also reduce the long-range magnetostatic coupling between the hard magnetic grains; both effects lead to an increase of the coercive field. The Kerr optical micrograph of Fig.1 shows the magnetic domain contrast inside the grains parallel to the alignment direction of the magnet. The formation of intermetallic, soft magnetic Nd-(Fe,S2) phases, such as the Laves type $Nd(Fe,S2)_2$-phase, deteriorate the coercivity of the magnets. If dopant elements M1 or M2 are added to Nd-Fe-B, generally the coercivity is increased and the corrosion resistance is improved. This is the case, if the Nd-rich intergranular phase is replaced by other phases, such as $AlNd_6Fe_{13}$ and $Nd_3Co$,

especially in large-grained magnets. Figure 2 is an TEM micrograph showing the additional intergranular $Al_1Fe_{13}Nd_6$ and $Nd_3Co$ phases in a Nd-(Fe,Co)-B:(Al,Mo) magnet. On the other hand, the decrease of the volume fraction of the hard magnetic phase within the magnet decreases the remanence.

The processing route of the magnet strongly influences the grain size and grain size distribution. The coercive field in sintered magnets strongly depends on the sintering parameters, such as temperature and time. Nanocrystalline and submicron magnets are obtained by the melt-spinning route, or by mechanically alloying, or by the HDDR process [11-13]. Hot pressing and die upsetting of Nd-Fe-B ribbon materials reveals a densely packed, anisotropic magnetic material. Platelet-shaped grains with diameters less than 1 micron are observed by TEM-investigations. The degree of orientation of the platelets, which are stacked transverse to the press direction with the easy c-axes perpendicular to the face of each grain, determines the remanence and coercive field of the magnet. These magnets are fully dense, and energy density product as large as 360 kJ/m$^3$ have been attained [14]. The degree of alignment, size and shape of the grains and the intergranular regions within the ribbons control the macroscopic magnetic properties. Die-upsetting modifies the spheroidal grains [15] after hot-pressing to platelets as shown in the TEM micrographs of Fig.3. Misaligned grains, which are clearly visible, deteriorate the remanence. The c-axis for each grain runs perpendicular to the straight elongated edge. Nd-rich phase is found among the platelet shaped grains as a fine layer between the straight edges or as pockets at the end of the platelets or between the misaligned and aligned grains. On the other hand the magnets with a lower remanence show a microstructure with more equiaxed grains. In most of the melt-spun magnets regions with abnormally grown, large grains were found. Some of these grains were fully developed, platelet shaped grains.

## 4. Highest energy density Nd-Fe-B magnets

Nd-Fe-B sintered magnets possessing outstanding magnetic properties have developed into a major permanent magnet material in the past 15 years since their invention. The drastic increase of the energy density product of newly developed $Nd_2Fe_{14}B$ based magnets enabled the invention of many new applications of permanent magnets. Applications of highest energy density magnets (> 400 kJ/m³), are expanding; voice coil motors for hard disk drives, magnetic resonance imaging, small sized motors, electrical devices and so on. These magnets are produced by a conventional powder metallurgical process which is essentially based on alloy-making, coarse-milling, pulverising, pressing in a magnetic field, sintering, heat-treatment and surface coating. In this process, it is very important to keep the processing atmosphere either in a vacuum or in an inert gas because rare earth elements easily oxidise. The theoretical maximum value of the energy density product is in the case of a perfectly squared demagnetisation curve given by:

$$\left(B \cdot H\right)_{\max}^{theor.} = \frac{1}{4 \cdot m_0} \cdot J_r^2 = \frac{1}{4 \cdot m_0} \cdot \left( J_s \cdot \frac{r}{r_0} \cdot V_{hm} \cdot \cos j \right)^2 \qquad (1)$$

$$\text{if} \quad \left| {}_J H_c \right| \geq \frac{1}{2 \cdot m_0} \cdot J_r \qquad (2)$$

where, $J_s$ is the saturation magnetisation of the hard magnetic phase (1.61 T), $V_{hm}$ and φ are the volume fraction and the degree of alignment of the hard magnetic grains, respectively. In order to enhance $J_r$ and therefore the energy density product, it is necessary to avoid pores and to densify the magnets up to the theoretical value, increase the volume fraction $V_{hm}$ and achieve a high degree of alignment φ. In anisotropic sintered magnets, the orientation of each grain from the easy direction of the magnet is usually described by the relation:

The theoretical value of the maximum energy product of $Nd_2Fe_{14}B$ based magnets is calculated to be 512 kJ/m³ assuming 100% perfect alignment and 100% volume fraction of the hard phase. The origin of this magnetic property lies in the $Nd_2Fe_{14}B$ ternary tetragonal compound as a main phase. In addition, according to the ternary Nd-Fe-B phase diagram this magnet contains also a certain amount of $Nd_{1.1}Fe_4B_4$-phase and a Nd-rich phase. which is essential for sintering with liquid phase. In order to densify the magnets up to the theoretical density, it is very important to control the composition of magnets thus generating sufficient amount of liquid phase at sintering.

Several authors have reported to obtain Nd-Fe-B based magnets with 400 kJ/m$^3$ energy density product by

- keeping the oxygen content low [16]
- using the powder mixing technique [17]
- increasing the magnetising field and reducing the pressure during compaction [18]

A new technology - Rubber isostatic pressing (RIP) - has been developed by Sagawa et al. [19,20] to improve the orientation of the particles in the green compact to obtain sintered magnets with perfect orientation. Rubber isostatic pressing (RIP) is one of the key technologies to approach for the theoretical limit of the magnets based on $Nd_2Fe_{l4}B$. In RIP, magnet powder is subjected to such a strong pulsed field just before the compaction that the powder in the rubber mold is thoroughly oriented. Then the powder is compacted isostatically, while the orientation is completely held. In the conventional die pressing which uses no rubber molds, the pressure applied to the powder is uniaxial. The uniaxial pressure tends to disturb the orientation of the particles during the pressing. To prevent this orientation disturbance, the powder has to be subjected to a strong magnetic field throughout the pressing
The high orientation of the magnet produced by RIP is attributed to:

- Application of a strong pulsed field which dissolves the agglomeration of the magnet powder particles, and then, impulsively orients the particles
- Isostatic pressing which holds the orientation high during the pressing

Magnets of the composition $Nd_{15.1-x}Fe_{78+x}B_6Cu_{0.03}Al_{0.7}$ [x= 0-2.5] were prepared by the powdermetallurgical sintering route [21]. The energy density product >400 kJ/m$^3$ and the coercive field of 800 kA/m were obtained after a combination of rubber isostatic and transverse die pressing methods under optimised sintering conditions. The misalignment of the hard magnetic grains with a diameter of 2~5 μm was calculated in the best case in the order < 14°. The high oxygen content of the magnets was gradually decreased from values of 4000 - 6000 ppm to a value < 1000 ppm. This high oxygen content was one limiting factor to decrease the Nd-content in order to improve the volume fraction of the hard magnetic phase.
The demagnetisation curves of two optimised magnets with a low and a high oxygen content and a composition of $Nd_{13.5}Fe_{bal}B_{5.95}Cu_{0.03}Al_{0.7}$ is shown in Fig.4. The magnets produced were sintered between 960°C and 1100°C. The sintering temperature was varied to get

optimum density (7.5~7.6 g/cm$^3$) and $(B.H)_{max}$. The density of the samples and the remanence increased with increasing sintering temperature keeping the sintering time constant (3 hours), while the squareness of the demagnetisation curve only partly increased and drastically decreased as abnormal grain growth of the 2:14:1 grains occurred [22]. Abnormal grain growth (AGG) of the 2:14:1 grains occurred preferentially in magnets with low oxygen content (Fig.5), thus the squareness of the demagnetisation curve drastically decreased. The oxygen content strongly affects the AGG and the magnets with higher oxygen content have the higher critical temperatures at which the AGG occurs. On the other hand, isotropic magnets tend to have the lower critical temperatures than anisotropic magnets by 10-20°C. A single or a two step (800°C plus quenching) annealing treatment at 500~600°C for 60 min increased the coercive field by about 200 kA/m or about 20%. Besides the density and coercive field also the squareness of the demagnetising curve has to be optimised in order to get highest values of energy density products.

The influence of oxygen on the hard magnetic properties is more complex. Kim et al [23] reported that a controlled doping with oxygen improved grain alignment and resulted in an increase in remanence, coercivity and loop squareness. Endoh and Shindo [18] reported about an energy density product of 410 kJ/m$^3$ of a low oxygen (< 2000 ppm) $Nd_{12.7}Fe_{81.3}B_6$ sintered magnet. One possibility to improve the alignment factor is to optimise the alignment field and/or pressure during transverse pressing. Even the sintering process influences the degree of alignment of the grains [24]. On the other hand several authors [20,25] found that the highest alignment is obtained by isostatic die pressing (φ=11-14°), followed by the transverse field die pressing (φ=18-20°)and the axial field die pressing (φ=25-27°).

## 5. Micromagnetic simulation of magnetic domain nucleation at grain boundaries

The coercive field is determined by the long range dipolar interaction and short range exchange coupling between neighbouring hard magnetic grains. The doping of elements changes the phase relation and favours the formation of new phases. Additional secondary non-magnetic intergranular phases decrease the remanence and interrupt the magnetic interactions between the grains, thereby improving the coercivity of large grained sintered magnets. For magnets with higher Nd-concentrations grain size, misorientation and distribution of grains control coercive field. Numerical micromagnetics help to understand the correlation between the intrinsic magnetic properties, the microstructure and the magnetic interaction that determines coercivity and remanence. The dipolar interactions considerably reduce the coercive field of ideally oriented particles with respect to ${}_JH_c$ of an isolated particle. Exchange coupling between misaligned grains drastically reduces the coercive field. The higher the Nd-content of the magnet and therefore the volume fraction of the Nd-rich intergranular phase is, the more reduced is the contribution of the exchange and also dipolar coupling between the grains.

The numerical simulation starts form the total magnetic Gibb's free energy $E_t$ which is the sum of the sum of the exchange, the magneto-crystalline anisotropy energy, the magnetostatic energy, and the Zeeman energy of the magnetic polarization in an external field $\boldsymbol{H}_{ext}$ [26]:

$$E_t = \int \left[ A \sum_{i=1}^{3} \left( \nabla b_i \right)^2 - K_1 (\mathbf{J} \cdot \mathbf{u})^2 - \frac{1}{2} \mathbf{J} \cdot \mathbf{H}_d - \mathbf{J} \cdot \mathbf{H}_{ext} \right] dV \qquad (3)$$

where $A$ is the exchange constant, $\boldsymbol{H}_d$ is the demagnetizing field, $K_1$ is anisotropy constant, and $\boldsymbol{u}$ denotes the unit vector parallel to the c-axis. When the direction cosines of the magnetization $b_i$ are approximated by piecewise linear functions on the finite element mesh, the energy functional (3) reduces to an energy function with the nodal values of the direction cosines as unknowns. Its minimization of with respect to the direction cosines of the magnetization at the nodal points variables, subject to the constraint $b_1^2 + b_2^2 + b_3^2 = 1$, provides an equilibrium distribution of the magnetization. To satisfy the constraint, the magnetization can be represented by polar coordinates. The resulting algebraic minimization problem is solved using a quasi-Newton conjugate gradient technique [27]. The demagnetising field $\boldsymbol{H}_d$ follows from the magnetic scalar potential which is calculated using a hybrid finite element / boundary technique [28].

Micromagnetic 3D finite element calculations were used to simulate the influence of Nd-rich phases located at grain boundary junctions, reduced anisotropy near the grain boundaries, and the degree of alignment on the nucleation of reversed domains. The numerical results show that all three effects are correlated and contribute in a complex way to the measured coercivity. The finite element models used for the simulations are based on TEM investigations. Figure 6a shows a TEM image of a grain boundary junction between three grains and a small amount of a Nd-rich intergranular phase. The 3D drawing of Fig.6b shows schematically the Nd-rich phase along grain boundary edges and the direct contact between the neighbouring 2:14:1-grains in the middle of the grain faces. Figure 7 shows the 3D model of the finite element model and the generated mesh near the junction of four neighbouring grains. For the calculations, the misalignment of the grains was varied from 8° to 16°.

The difference in the intrinsic magnetic properties between the bulk of the grains and the grain boundary region is taken into account. For a perfect microstructure the numerical results agree well with the Stoner-Wohlfarth theory. The most misoriented grain, which has the largest angle between the c-axes and the alignment direction, determines the coercive field. The coercive field decreases with increasing misalignment. A reduction of the magneto-crystalline anisotropy near the grain boundaries leads to a linear decrease of the coercive field. The coercive field decreases from 3200 kA/m to 900 kA/m as the anisotropy constant in a 6 nm thick region near the grain boundaries is reduced from its bulk value to zero. The reduction in the magneto-crystalline anisotropy reverses the dependence of the coercive field on the degree of alignment. The coercive field increases by about 80 kA/m as the misalignment angle is changed from 8° to 16°. This effect has to be attributed to a higher demagnetising field in the well aligned sample which initiates the nucleation of reversed domains into the defect region. The coercive field of Nd-Fe-B sintered magnets increase with increasing Nd content [29]. The finite element simulations confirm that non-magnetic Nd-rich phases at grain boundary junctions significantly increase the coercive field. The coercive field increases by about 15% as a non-magnetic Nd-rich phase near grain boundary junctions is taken into account. The simulations show that the presence of the Nd-rich phase significantly changes the exchange and the magnetostatic interactions. As a consequence the nucleation of reversed domains is suppressed. The simulations allow to identify the regions within the microstructure where reversed domains are nucleated (Fig.8). The comparison with experimental data provides a detailed understanding of magnetization reversal in high energy density permanent magnets. The demagnetisation curves of Fig.9 compare perfect grain boundaries, distorted grain boundaries and experimental data. The influence of the magnetocrystalline anisotropy of the intergranular region on the coercive field is clearly shown. The simulations explain experimental data [23] which show a decrease of the coercive field with increasing misalignment for high-coercive, Dy-containing Nd-Fe-B magnets, whereas a slight increase of

coercivity with misalignment is observed in Dy-free Nd-Fe-B magnets. This effect may be attributed to a „surface hardening“ of by the addition of Dy or Tb elements. Similar numerical results were obtained by Bachman et al [30], who used a finite element method combined with an atomic exchange interaction model based on the Heisenberg model for localized interacting magnetic moments and found a decrease of the intrinsic coercivity with an increase in the degree of the grain misalignment assuming a perfect grain boundary. In order to obtain an accurate results for the magnetization near the grain boundary, Bachman et al combined an atomistic calculation with a continuous finite element model. Thus it was possible to predict the arrangement of the magnetic moments within the grain boundary and the resulting coercive field precisely.

Soft magnetic secondary phases, such as α-Fe, destroy coercivity in large grained magnets. Numerical, micromagnetic calculations have shown that the critical diameter for the curling process of the polarisation vector inside the α-Fe phase, embedded between hard magnetic grains, is about 90 nm. This is the reason why the formation of large soft magnetic grains considerably reduces the coercive field [31].

The coercive field of high performance Nd-Fe-B based magnets is determined by the high uniaxial magnetocrystalline anisotropy as well as the magnetostatic and exchange interactions between neighbouring hard magnetic grains. The dipolar interactions between misaligned grains are more pronounced in large-grained magnets, whereas exchange coupling reduces the coercive field in small-grained magnets.

## 6. Conclusions

Microstructural parameters, such as grain size, shape of grains, crystal structure, crystal defects, orientation and composition of various phases, were investigated by means of analytical and high resolution electron microscopy. The complex microstructure considerably influences the magnetic reversal process. Special attention was laid on determining the role of intergranular phases on the coercive field of the magnets. The Nd-rich intergranular phase is necessary for the liquid phase sintering process, but deteriorates the corrosion stability and reduces the remanencs. Detailed TEM analysis revealed various additional binary and ternary phases in the intergranular region between hard magnetic grains doped and substituted Nd-Fe-B magnets.

The investigation of high remanence and low Nd-content sintered magnets obtains Nd-rich phases only at grain boundary junctions. In order to improve coercive field, remanence and energy density, it is necessary to increase the volume fraction of the hard magnetic phase by decreasing the amount of oxygen, Nd and pores, and to improve the degree of alignment of the $Nd_2Fe_{14}B$ grains. Oxygen is partly dissolved in the Nd-rich intergranular phase. Reducing the amount of oxygen (< 1000 ppm) the problem of abnormal grain growth during sintering becomes more severe.

The quantitative interaction between magnetisation and microstructure has been calculated by means of a micromagnetic finite element technique. Our micromagnetic simulations of the magnetization reversal process revealed exact predictions of the influence of intergranular phases on the coercive field: Nd-rich phases at grain boundary junctions reduce the effective coupling between the grains an thus increase the coercive field up to 15 percent. Perfect grains without any reduction of the magnetocrystalline anisotropy show a behaviour which is

expected from the Stoner-Wohlfarth theory. The coercive field decreases with increasing misalignment. Defects at the surface reduce the magnetocrystalline anisotropy locally and thus drastically decrease the coercive field. Then the coercive field shows only weak dependence on the degree of alignment. The defects change the local effective fields and thus reverse the behaviour observerd for perfect grains: A better alignment slightly reduces the coercive field.

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**Literature**

[1] K. J Strnat, Hoffer, G., Oson , J. and Ostertag W., 1967, J. Appl. Phys. 38, 1001.
[2] M. Sagawa, Fujimura, S., Togawa, N., Yamamoto, H. and Matsuura, Y., 1984, J. Appl. Phys. 55, 2083.
[3] J.J. Croat, Herbst, J.F., Lee, R.W. and Pinkerton F.E., 1984, J. Appl. Phys. 55, 2078.
[4] J.F. Herbst and Croat, J.J. (1991), JMMM 100, 57.
[5] J. Fidler and Schrefl, T. (1996), JAP 79,5029.
[6] T. Schrefl and J. Fidler, J.M.M.M. 177-181 (1998) 970-975.
[7] J. Bernardi, Fidler, J. and Födermayr,F., 1992, IEEE Trans. Magn. 28, 2127.
[8] J Bernardi and Fidler, J., 1994, J. Appl. Phys. 76, 6241.
[9] Y. Hirose, H. Hasegawa, S. Sasaki and M. Sagawa,
Proc. XV. Workshop on RareEarth Magnets and Applications, Dresden, 1998, Vol1., p.77-96.
[10] J Fidler, "Rare earth intermetallic magnets", Inst.Phys.Conf.Ser.No.152, Section G: Magnetic Materials, Paper presented at the 11th Int. Conf. on Ternary & Multinary Compounds, ICTMC-11, Salford, UK, September 1997, (1998), 805-813.
[11] I. R Harris, 1992, Proceedings of the XII. International Workshop on Rare Earth Magnets and their Appl., ed. by B.Street, The University of Western Australia, 347.
[12] R. Nakayama, Takeshita, T., Itakura, M., Kuwano, N. and Oki, K., 1994, JAP. 76, 412.
[13] M. Uehara, Tomizawa, H., Hirosawa, S., Tomida, T. and Maehara, Y., 1993, IEEE Trans. Magn. 29, 2770.
[14] J.J. Croat, J. Less-Common Met., 148, 7 (1989).
[15] R.K. Mishra, J. Appl. Phys., 62, 967 (1987).
[16] M. Sagawa, S. Hirosawa, H. Yamamoto, S. Fujimura and Y. Matsuura, Jpn. J. Appl. Phys., 26 (1987) 785.
[17] E. Otsuki, T. Otsuka and T. Imai, Proc. 11th Int. Workshop on rare earth magnets and their applications, Pittsburgh, ed. by Shankar, Vol.1, (1990) 328.
[18] M. Endoh and M. Shindo, Proc. 13th Int. Workshop on rare earth magnets and their applications, Birmingham, ed. by Manwaring et al, Vol.1, (1994) 397.
[19] M. Sagawa and H. Nagata, IEEE Trans Magn. 29 (1993) 2747.
[20] M. Sagawa, H. Nagata O. Itatani and W. Watanabe, Proc. 13th Int. Workshop on rare earth magnets and their applications, Birmingham, ed. by Manwaring et al, Suppl., (1994) 13.
[21] S. Sasaki, PhD Thesis, Vienna University of Technology, Austria, 1999.
[22] W. Rodewald, B. Wall and W. Fernengel, IEEE Trans. Magn. 33 (1997) 3841.
[23] A.S. Kim, F.E. Camp and H.H. Stadelmaier, J. Appl. Phys. 76 (1994) 6265.
[24] T.S. Chin, M.P. Hung, D.S. Tsai, K.F. Wu and W.C. Chang, J. Appl. Phys. 64 (1988) 5531.

[25] W. Fernengel, A. Lehnert, M. Katter, W. Rodewald and B. Wall, J.M.M.M., 157/158(1996) 19.
[26] W. F. Brown Jr., Micromagnetics (Wiley, New York, 1963).
[27] P. E. Gill, W. Murray, and M. H. Wright, Practical Optimization (Academic Press, London, 1993).
[28] D. R. Fredkin and T. R. Koehler, IEEE Trans. Magn. 26, 415-417 (1990).
[29] S. Hirosawa and Y. Kaneko, Proceedings 15th Int. Workshop on Rare-Earth Magnets and theirApplication, Dresden, Germany, p. 43 (1998).
[30] M. Bachmann, R. Fischer and H. Kronmueller, Proc. X. Symposium on magnetic anisotropy and coercivity in rare earth transition metal alloys, Dresden 1998, 1. 217-236,
[31] Thomas Schrefl and Josef Fidler, „Micromagnetics of nanocrystalline permanent magnets“, MRS-99 Proceedings of the Symposium I: Amorphous and Soft magnetic materials for Hard and Soft Magnetic Applications, April 1999.

**Figure Captions**

Fig.1: Kerr optical micrograph showing the magnetic domain contrast inside the grains parallel to the alignment direction of the optimised Nd-Fe-B magnet. The average grain size is in the order of 2- 5 microns.

Fig.2: TEM micrograph showing the additional intergranular $Al_1Fe_{13}Nd_6$ (iAL) and $Nd_3Co$ (iNc) phases besides the $Nd_2(Fe,Co)_{14}B$ ($\Phi$) phase in a Nd-(Fe,Co)-B:(Al,Mo) magnet

Fig.3: TEM micrographs of a hot pressed and die-upset $Nd_{14}Fe_{72}Co_7B_6Ga1$ magnet with $J_r$=1.32 T, ${}_JH_c$=1240 kA/m (perpendicular to c-axis view).

Fig.4: Comparison of demagnetisation curves of $Nd_{13.5}Fe_{bal}B_{5.95}Cu_{0.03}Al_{0.7}$ sintered magnets manufactured by rubber isostatic die pressing (RIP) and transverse die pressing on air (TDP).
(A) $J_r$=1.505 T, $(B.H)_{max}$= 432 kJ/m$^3$
(B) $J_r$=1.406 T, $(B.H)_{max}$= 333 kJ/m$^3$

Fig.5: Scanning electron micrograph of a fractured surface showing the abnormally grown grains in a low oxygen (< 1000 ppm) $Nd_{13.7}Fe_{bal}B_{5.95}Cu_{0.03}Al_{0.7}$ magnet sintered at 1000°C / 3 hours.

Fig.6: TEM image of a grain boundary junction of a $Nd_{13.7}Fe_{bal}B_{5.95}Cu_{0.03}Al_{0.7}$ sintered magnet with $(B.H)_{max}$= 432 kJ/m$^3$ (a). c-axis of grains is perpendicular to the image plane. A sketch of the 3D grain surrounded by a Nd-rich phase at grain edges is shown in (b).

Fig.7: 3D model of the finite element model and the generated mesh near the junction of four neighbouring grains. For the calculations, the misalignment of the grains was varied from 8° to 16°.

Fig.8: Finite element simulations allow to identify the regions within the microstructure where reversed domains are nucleated at $H_{ext}$=960 kA/m. The nucleation of reversed domains starts in the intergranular region assuming $K_1$=0.

Fig. 9. Effect of the magnetocrystalline anisotropy of the intergranular region between the $Nd_2Fe_{14}B$ grains on the demagnetisation curve and coercive field compared with experimental data.